

## Discovery of Non-Aroclor PCB (3,3'-Dichlorobiphenyl) in Chicago Air

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Air samples were collected in Chicago, Illinois in 2007, and 3,3'-dichlorobiphenyl (PCB11, CAS 2050-67-1) was detected and quantified using GC/MS/MS in 91% of 184 samples. To the best of our knowledge, this is the first published report of PCB11 in ambient air. This compound is ubiquitous in air throughout the city of Chicago. The annual mean concentration in air samples collected from November 2006 to November 2007 is  $24 \text{ pg m}^{-3}$  ( $\pm 24 \text{ pg m}^{-3}$  SD), although the seasonal variation is significant. The concentration of PCB11 is up to 15% of measured polychlorinated biphenyls (PCBs) in air but only up to 0.16% of commercial Aroclor mixtures that were banned from production in the 1970s. PCB11 is associated with pigments, paints, and resins and has been reported to be a dominant congener among PCBs detected in the wastewater effluent from paint production. The wide distribution of PCB11 in Chicago air is consistent with volatilization of this compound from painted surfaces although the actual source of PCB11 is unknown.

### Introduction

Polychlorinated biphenyls (PCBs) are a set of 209 compounds (congeners) that were extensively manufactured between the late 1920s and the 1970s (1). PCBs were primarily marketed as mixtures called Aroclors by Monsanto Chemical Company until production ceased in the United States in the late 1970s (2). They are regulated under the Toxic Substances Control Act in part because of their probable carcinogenicity and tendency to bioaccumulate in the foodweb (1, 3–5). There are no known natural sources of PCBs in the environment, although some PCBs can be produced from other PCBs via microbial decay (6). Since the 1970s, many studies have shown that the concentration of PCBs associated with Aroclors has decreased in humans, animals, and the environment. It has been assumed that PCBs would eventually be virtually eliminated (7).

During a field study of PCBs in urban Chicago air, we unexpectedly found a PCB congener, 3,3'-dichlorobiphenyl (PCB11), that was not produced as an Aroclor in the environment. PCB11 is believed to be formed during production of diarylide yellow and other pigments from 3,3'-dichlorobenzidine (Figure 1) (8–10). Here, we report the discovery and prevalence of this non-Aroclor PCB in air samples collected throughout the city from November 2006 to November 2007. The detection of PCB11 could have

important impacts on regulatory decisions in the future, although its source, toxicity, and potential for human exposure need further investigation.

### Materials and Methods

**Air Sampling.** Air was sampled using high-volume air samplers (Hi-Vols) equipped with quartz fiber filters and XAD-2 resins. Hi-Vols were mounted on platforms attached to the rear of two medical clinic vans (Figure 2). The Hi-Vol platforms were designed to raise the sampler to the top of the van for operation and lower the sampler for filter and XAD replacement.

The sampling locations (Table S1) were primarily elementary schools where the mobile clinics provide service to the students and their families for diagnosis and treatment of asthma and related respiratory illness. When the vans visited the schools for clinical service, the Hi-Vols collected air samples for the 6–8 h period that the van remained at the school. The samplers were operated with the assistance of the trained staff at Mobile C.A.R.E. Foundation of Chicago (Comprehensive Care for Chicagoland's Children with Asthma). Both vans went out for clinical service usually on the same day so two samples were collected at two different sites on most sampling days. The air was pulled with a vacuum pump through a quartz fiber filter to retain particles and then through an XAD-2 resin cartridge to collect PCBs in the gas phase. Temperature and relative humidity were recorded every 5 min on one van by the CR800 measurement and control system (Campbell scientific, inc., Logan, UT). The flow pressure drop was recorded daily using a magnehelic pressure gauge mounted on each sampler.

**Sample Analysis.** After collection, all samples were placed in sealed ziplock bags and stored in a refrigerator until shipped to the laboratory. Once the samples were transported to the laboratory, they were logged and stored at  $4^\circ\text{C}$  until extracted. The filter and XAD were extracted by accelerated solvent extraction (ASE 300, Dionex, Sunnyvale, CA) using an optimized EPA Method 3545 (11). The extraction cell was preheated for 5 min to  $100^\circ\text{C}$ , followed by a static extraction for 5 min at a pressure of 10,000 kPa. The extraction solvent was acetone/hexane (1:1, v/v). Prior to extraction air samples were spiked with surrogate standards containing 3,5-dichlorobiphenyl (PCB14), 2,3,5,6-tetrachlorobiphenyl (PCB65), and 2,3,4,4',5,6-hexachlorobiphenyl (PCB166). The resulting extracts were further reduced to about  $500 \mu\text{L}$  by a Turbovap concentration workstation, and the final solutions were spiked with the internal standard containing 2,2',3,4,4',5,6,6'-octachlorobiphenyl (PCB204) prior to analysis. All glassware was combusted overnight at  $450^\circ\text{C}$  to remove any traces of organic compounds prior to use during the analysis.

All samples were measured for a suite of 209 PCB congeners using a method similar to EPA method 1668A (12). The quantification of PCB homologues was performed by GC/MS/MS with an Agilent 6890N gas chromatograph with an Agilent 7683 series autosampler coupled to a Waters Micromass Quattro micro GC mass spectrometer (Milford, MA) operating under electron impact (EI) positive mode at 70 eV, in multiple reaction monitoring (MRM), and trap current  $200 \mu\text{A}$ . The retention windows were defined by PCB homologue parent and daughter ions. For PCB11 and other dichlorobiphenyls, the parent/daughter ion pair is 222/152.10. Two microliters of the sample was injected in splitless mode in a Supelco SP-Octyl fused silica capillary column ( $30 \text{ m} \times 250 \mu\text{m}$  i.d.  $\times 0.25 \mu\text{m}$  film thickness) with helium as carrier gas at a constant flow rate of  $0.8 \text{ mL min}^{-1}$ . The

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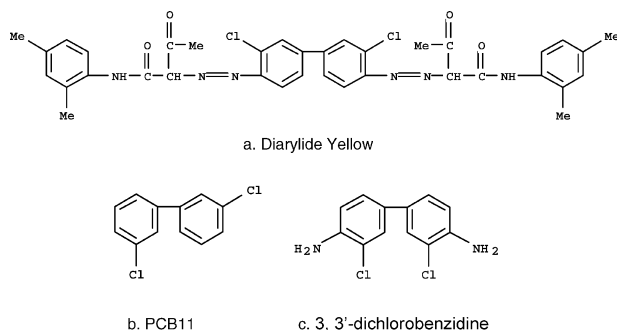


FIGURE 1. Molecular structures.

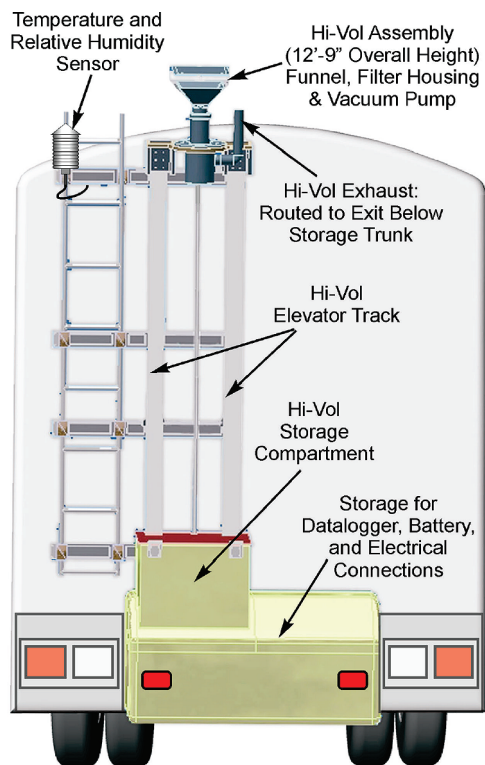


FIGURE 2. Vehicle-mounted high-volume air sampling system.

collision gas was ultra pure carrier grade Argon. The initial oven temperature was 75 °C which was held for 5 min. The gradient program ran to 150 at 15 °C per minute and was held for 1 min. The second step of the gradient ran to 280 at 2.5 °C per minute and was held for 3 min. The method separated the 209 congeners into 169 peaks. PCB11 was completely separated from other congeners with no interferences (Figure 3).

The quality of the data set was assured through analysis of field blanks, use of surrogate PCB standards in every sample, and replicate (side-by-side) analyses. The concentration of PCB11 was less than the method detection limit (MDL,  $\sim 1.0 \text{ pg m}^{-3}$ ) in 14 field samples and in 18 solvent blanks. The recoveries of PCB14, PCB65, and PCB166 surrogate standards were  $95 \pm 11\%$ ,  $100 \pm 18\%$ , and  $105 \pm 14\%$ , respectively. PCB congener concentrations were not corrected for surrogate recoveries and blank levels. On four occasions, the air samplers were operated when the two vans were parked near each other. The average relative percent difference for PCB11 in these eight samples was 30.1% with standard deviation of 27.8%.

## Results and Discussion

Air samples were collected using an innovative sampling strategy of vehicle-mounted high-volume air samplers at

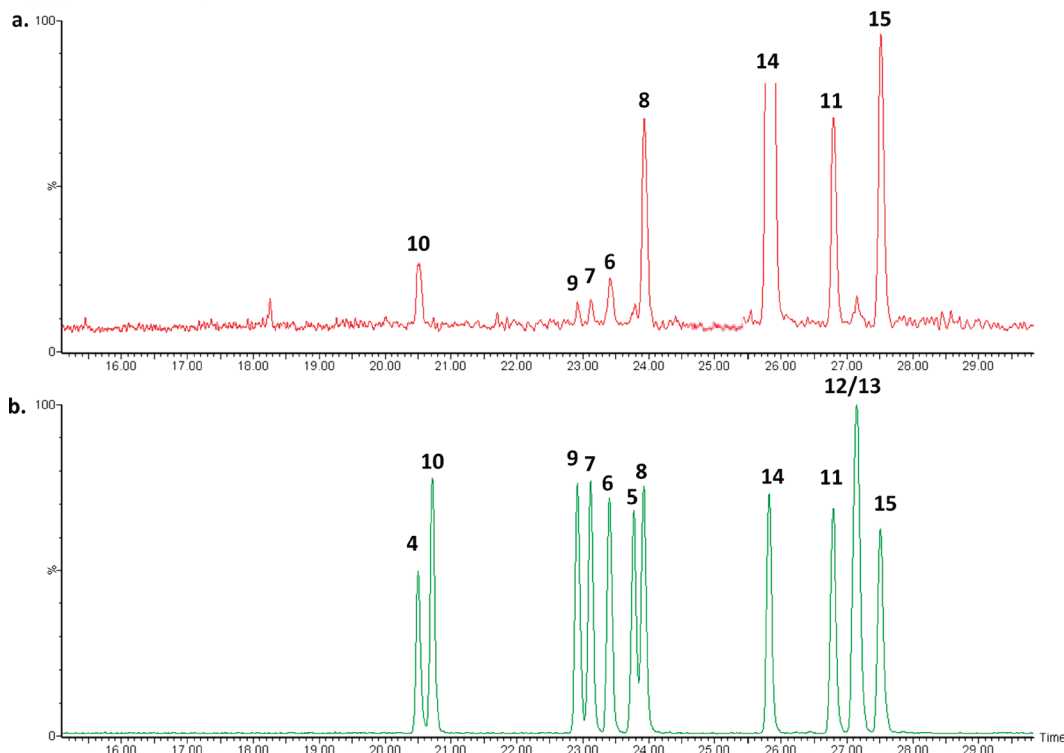
more than 37 sites throughout Chicago, Illinois in 2007. We measured 209 PCB congeners in air with a range of the total PCB concentration from 75 to  $5,500 \text{ pg m}^{-3}$  with the annual average of  $835 \text{ pg m}^{-3}$  (SD  $940 \text{ pg m}^{-3}$ ). PCB11 is one of the PCB congeners we observed most often in Chicago air sample set, and among the most concentrated. PCB11 concentrations and associated average temperature during the sampling in the air sample set are listed in Table S2. It is detected in 91% of the 184 samples. On average, PCB11 is about 5% of the total PCB congeners in the Chicago air samples. In some samples, PCB11 comprises up to 15% of the total PCBs measured. When calculated by mole fraction, it is the fifth highest congener found in an average air sample (Figure 4).

The concentration of PCB11 in our sample set varies by season and ranges from nondetectable to  $140 \text{ pg m}^{-3}$ . Because PCBs are semivolatile and their concentrations are generally temperature dependent, the concentration is highest in the summer ( $48 \pm 28 \text{ pg m}^{-3}$  SD) and lowest in the winter ( $5.4 \pm 4.9 \text{ pg m}^{-3}$ ). This trend has been reported many times for PCBs in remote and urban areas (13). The natural logarithm of the concentration of PCB11, expressed as partial pressure, is linearly related to the inverse of temperature in Kelvin (Figure 5). The slope of the line is  $-6,300$  ( $R^2 = 0.66$ ), which is in agreement with the ranges for PCBs ( $-5,030 \pm 1,070$  SD) reported for samples collected by the Integrated Atmospheric Deposition Network (IADN) U.S. sites (13). The strong relationship between concentration and temperature suggests a volatilization source of the compound although it does not fully explain the variation. The concentration of PCB11 varies across the city, although not as much as do total PCBs. After normalizing for temperature at 288 K (13), the concentrations of PCB11 in the city varied from nondetectable to  $72 \text{ pg m}^{-3}$ . When all the samples collected at each site are averaged (excluding nondetects), the resulting temperature-normalized PCB11 concentrations vary by less than a factor of 10 (Figure 6).

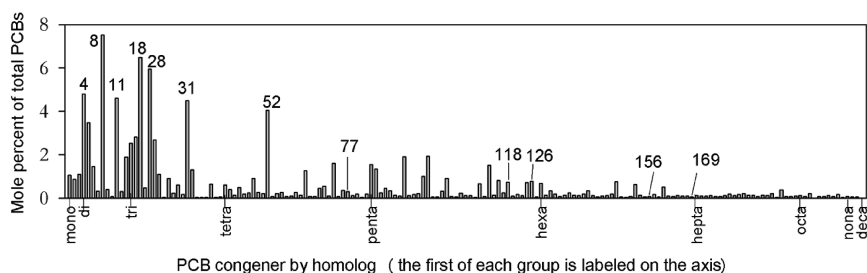
Theoretically, there are 209 PCB congeners that can be created during PCB manufacturing by catalytic chlorination of biphenyl. About 140–150 of these congeners are observed in the commercial mixtures (14). PCB11 is reported to be nondetectable ( $<0.05\%$ ) in most Aroclor mixtures except in Aroclor 1221, where PCB11 is as high as 0.16% (14, 15). Using our analytical method, we found less than 0.08% PCB11 in Aroclors 1016, 1242, 1254, and 1221. This indicates that the high level of PCB11 detected in the environment is not directly derived from commercial Aroclor products.

Non-Aroclor PCB congeners including PCB11 can be produced through reductive dechlorination (16). Zanaroli et al. found that PCB11 is one of the major metabolites of PCBs 77, 118, 126, 156, and 169 in spiked Venice Lagoon sediment microcosms (17). Rhee et al. also reported PCB11 was the only metabolite of PCB77 in Hudson River sediment incubations (18). However, none of the potential precursors to PCB11 are primary components in any Aroclor mixtures. Although they are all present in Chicago air, the relative concentration is low (Figure 4). Therefore, the high level of PCB11 in air is not likely due to microbial dechlorination of Aroclor PCB congeners (19, 20).

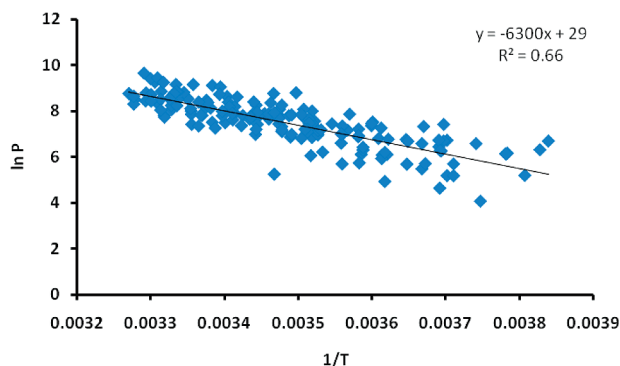
PCB11 has been reported in water or sediment samples collected downstream of industrial wastewater effluents and been identified in the waste from paint and pigment manufacturing facilities and as a byproduct of 3,3'-dichlorobenzidine which is used in yellow paint pigments (21). Litten et al. reported PCB11 in the New York/New Jersey Harbor, where it was more than 90% of the total PCBs in effluent from a wastewater treatment plant (20). King et al. reported the presence of PCB11 in water, sediments, suspended particulate materials, and biota in the Halifax Harbour (19). Both of these studies were conducted near waste effluent from paint and pigment manufacturing.



**FIGURE 3.** Multiple reaction monitoring chromatograms for the 222/152.10 ion pair: (a) a representative air sample and (b) calibration standard. The numbers on the tops of peaks represent the PCB number. PCB14 is a surrogate standard.



**FIGURE 4.** Mean distribution of PCB congeners in the Chicago gas-phase air samples.



**FIGURE 5.** Atmospheric concentrations (expressed as natural logarithm of partial pressure in atmospheres) of gas-phase PCB11 correlated with ambient temperature (K).

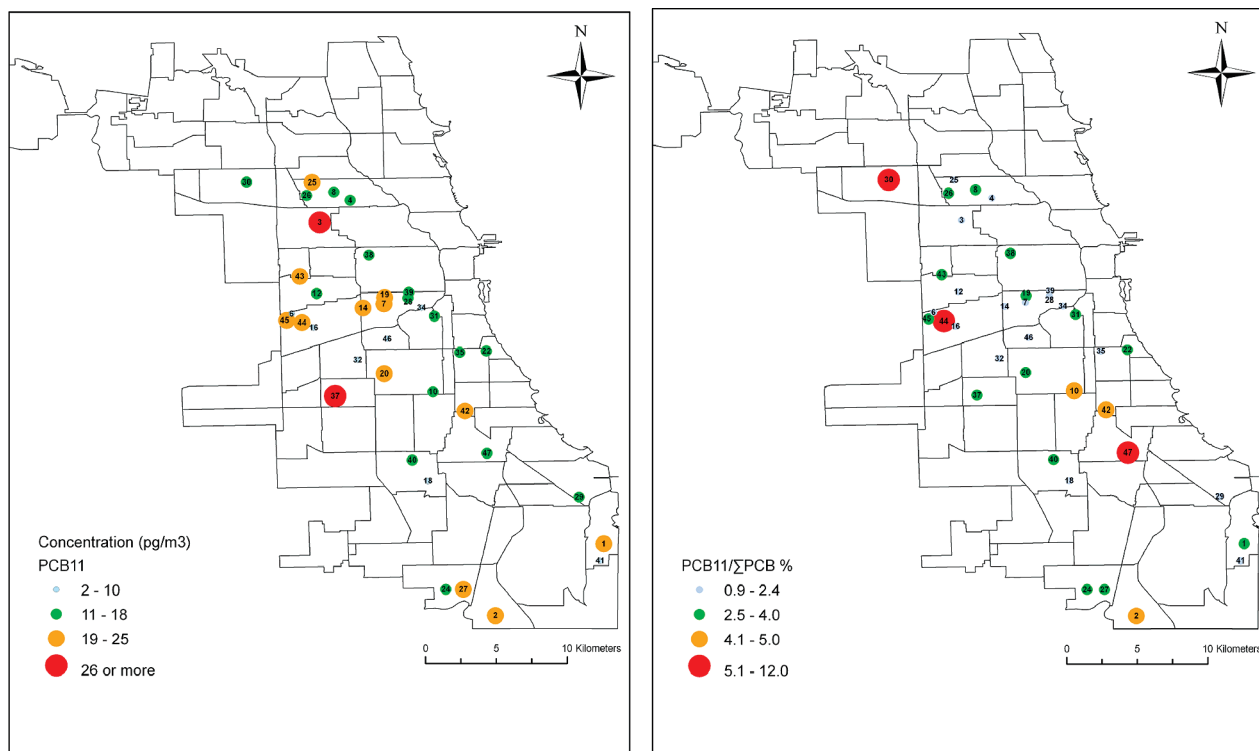
Recently, Du et al. detected PCB11 in the Delaware River and hypothesized it was from wastewater treatment plants (WWTP) effluents although there were no recorded dye manufactures in that area (22). These studies also used the SP-Octyl capillary column and either tandem mass spectrometry or high resolution mass spectrometry.

The Toxic Substances Control Act (TSCA) allows small concentrations of PCBs in products when their presence is due to inadvertent production of non-Aroclor PCBs or

recycling of Aroclor PCBs under limited circumstances (2). The TSCA regulation allows air emission of inadvertently generated PCBs at concentrations of less than 10 ppm (92 mg m<sup>-3</sup> of PCB11) and higher concentrations of mono- and dichlorinated PCBs, although industries that do so must report to the EPA. No industries in Chicago report emissions of PCBs to the EPA. While it is likely that paint and pigments are a source of PCB11, it is difficult to link high-concentration regions to proximity to paint and pigment facilities because there are more than 50 facilities with Standard Industrial Classification (SIC) codes indicating paint and pigment production and related activities. These facilities are widely distributed in Chicago (Figures S1–S6). It is possible that many such facilities have been releasing low levels of PCB11 for many years.

Since PCBs have been measured in Chicago air before, our new finding is probably due only to the uncommon analytical method employed in this study (23–25). The SP-Octyl capillary chromatography column separates different congeners, particularly those without *ortho*-chlorinated PCBs, than the more commonly used nonselective columns. In addition, the multiple reaction monitoring mode in GC/MS/MS is much more selective for PCBs than the more commonly used electron capture detection. Furthermore, many studies choose a small set of PCB congeners as representative of the





**FIGURE 6.** Annual average temperature-normalized concentration of gas-phase PCB11 (left) and the annual average percent of PCB11 of the total PCB congeners (right). The boundaries of communities identified under the 2004 U.S. Census within the city of Chicago are shown. The numbers on the maps are site names. Details for each site are described in the Supporting Information.

total. Using such a protocol eliminates the chance of detecting an unexpected congener.

The number and placement of chlorine atoms on biphenyl determine not only the physical–chemical characteristics of PCBs, but also their adverse biological effects. Among these, carcinogenicity, immunosuppression with thymic atrophy, edema, hyperkeratosis, hepatotoxicity, and others have been identified in human and animal studies (1, 26). Among the 209 PCB congeners, 12 coplanar congeners have been identified by the World Health Organization (WHO) as having dioxin-like toxicity, while multiortho-substituted PCBs have other mechanisms of toxicity (1, 28–30). PCB11, with only two chlorines, does not appear to display a receptor-driven toxicity, but rather may be a substrate for metabolic activation, although we know of no studies that have specifically evaluated the toxicity of this congener. However, recent studies have demonstrated that reactive metabolites of lower chlorinated PCBs in vitro and in vivo act as potential mutagens (28–30). For example, quinoid metabolites of PCB 3 were identified as potential ultimate mutagen in mammalian cells (29) and in animals (30).

The distribution of PCB11 throughout residential areas of Chicago suggests that the compound is a historical or current component of consumer paint products. The historical trend for PCB11 is unknown and probably different from that for Aroclors, particularly if PCB11 is produced as a byproduct of current paint manufacturing. Aroclor-PCBs in the environment are decreasing worldwide but this may not be the case for PCB11. The prevalence of PCB11 in Chicago air suggests that there are either multiple current sources in the city or that this compound is ubiquitous in background air. This has important implications for human exposure to this potentially toxic compound. While inhalation is not widely considered to be a major exposure route for higher molecular weight PCBs, it may be an important route for PCB11. Not only is PCB11 one of the most volatile PCBs, if it is present in interior paints indoor concentrations may be much higher than reported here. Consumption of paint chips

also could be a direct exposure route for children. It is also possible that PCB11 is present not only in Chicago, but in air elsewhere and also in fish, soil, water, food, and humans.

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## Supporting Information Available

Two tables and six figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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